COATINGS. ENAMELS

UDC 621.794:546.82:666.293

TREATMENT OF TITANIUM SURFACE BEFORE APPLYING DENTAL ENAMEL COATING

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Translated from Steklo i Keramika, No. 7, pp. 29 – 30, July, 2002.

A method for treating the surface of titanium and its alloys before the application of dental enamels is proposed. The effect of the surface treatment and a protective atmosphere on the strength of adhesion on the enamel – titanium interface and the rate of oxidation of titanium in heating is analyzed. It is demonstrated that the use of phosphoric acid as a pickling agent and the introduction of an additional degreasing operation increase the strength of adhesion of titanium to the enamel and decrease the rate of formation of an oxygen-rich layer on the metal surface.

Orthopedic stomatology increasingly uses titanium and titanium alloys with high bioinertness [1]. Various coatings, in particular glass ceramic enamels, are applied to improve the outward appearance and biocompatibility with living tissues.

One of the main conditions for getting a high-quality adhesive layer is the adhesion of enamel to titanium, which to a large extent depends not only on the composition of the enamel but on the purity of the metal surface as well. Preparation of the surface of titanium and its alloys before applying enamel coating primarily consists in the removal of the upper layer contaminated by incorporated elements (oxygen, hydrogen, nitrogen, etc.) [2]. There are many methods for treating the surface of titanium and its alloys before enamel deposition (U.S. patent No. 5476552) [3].

The usual pickling agents are composites of complex and expensive organic reactants having increased toxicity (isopropyl alcohol, alpha-naphthol, etc.). The main disadvantage of this methods is the fact that they do not take into account the specifics of application of dental enamel in layers, each of which is subjected to thermal treatment. There are usually 3 to 5 layers.

It is demonstrated in [4] that as a result of reducing reactions, silicides as well as titanium oxides emerge on the titanium-coating interface:

$$8Ti + 3SiO_2 = 3TiO_2 + Ti_5Si_3; \quad (1)$$

$$5Ti + 3SiO_2 = Ti_5Si_3 + 6O\uparrow. \quad (2)$$

The oxides together with the silicides and the vitreous phase form the adhesive layer. As the duration of exposure to thermal treatment increases, the reaction products (Ti_5Si_3, TiO_2, TiO) are accumulated in the contact zone of titanium with the coating, which weakens the adhesion and causes gradual scaling of the coating.

It is known [5] that there are different dependences of the titanium oxidation rate on the treatment duration in different temperature ranges. Thus, the temperature dependence of the oxidation in the temperature interval of 350 – 650°C is described by a logarithmic or cubic law, whereas a parabolic dependence is registered in the temperature interval of 650 – 850°C, and a linear dependence prevails in the interval of 850 – 950°C. In the latter case a loose porous oxide layer in formed, which is loosely fixed to the titanium surface.

The purpose of our study is to develop a simple method for preparing the surface of titanium and its alloys before applying dental enamel, taking into account the specifics of its application.

The studies were carried out on samples cut out from a plate of titanium VT1-00 2 mm thick. The coating was made from a mixture developed for dental coating on titanium, which contained silicon, aluminum, boron, titanium and other oxides (RF patent No. 21326772). The slip was deposited with a brush in 1 – 2 layers, consecutively drying each layer. Since the above-mentioned specifics of titanium oxidation restrict the range of applicable temperatures, under which an oxide layer firmly fixed to the metal is formed, the heat treatment was carried out at 750 and 790°C in a SNOL muffle furnace in an air atmosphere and in an Averon automated furnace in air and in vacuum. The titanium sample with a deposited enamel coating was inserted into a preheated muffle furnace ensuring a virtually instant tempera-

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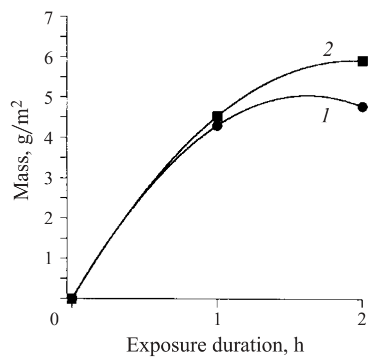

Fig. 1. Time dependence of the weight increment in samples of alloy VT-6 at 750°C without treatment (*1*) and after phosphating (*2*).

ture rise up to 750°C in an air atmospheres or into the Averon furnace, whose heating was limited to a rate of 80 K/min. In the latter case the time of stay at a temperature above 500°C was significantly longer. The working space of the furnace was evacuated at 360°C and refilled with air only after the end of the heat-treatment procedure and the furnace cooling at least to 700°C.

The thickness of the oxidized titanium layer was measured with a Neophot-32 optical microscope on microsections pickled with a 2% solution of hydrofluoric acid. The photos of the microsections were taken with a Neophot-21 optical microscope at magnification of 500 times. The strength of adhesion was estimated based on the shear strength determined on an Instron-11.95 tensile-testing machine. The testing was performed on overlapping samples glued with the enamel composition [6]. The samples were locked in the clamps of the tensile-testing machine and loaded at a constant rate until destruction of the sample.

Mechanical treatment and chemical pickling before enameling [3] provides for better wettability of the titanium surface with respect to the enamel melt. The pickling agent was phosphoric acid [7] of density 1.25 – 1.30 g/cm^3. Pickling was carried out at a temperature of 40 ± 5°C for 45 min, after which the surface was washed in distilled water until the phosphate ions disappeared. Treatment of a cleaned titanium surface with pickling agents containing phosphoric acid or phosphate not only improves the adhesion to the metal but also passivates the titanium due to the formation of insoluble compounds which prevent the penetration of oxygen into the metal. Earlier [8] it was demonstrated that during a 2-h heat treatment at 750°C in an air atmosphere the weight increment of a sample made of titanium alloy VT-6 passivated by phosphoric acid amounted to 4.77 g/m^2, and that of a non-treated sample was 5.90 g/m^2 (Fig. 1).

For a more complete and appropriate preparation of titanium surface, an additional operation, namely degreasing, was performed before pickling. It was carried out for 5 min in acetone with subsequent drying in air. The strength of adhesion of titanium and the enamel coating on samples not treated in acetone was registered to be 2.17 MPa, and that of the samples treated in acetone was 2.52 MPa.

TABLE 1

Heat treatment conditions		Number of enamel coats	Thickness of oxidized layer, μm
exposure duration, min	atmosphere		
2	Vacuum	1	3.4
3	The same	1	7.0
4	"	1	10.0
4	Air	1	1.9
6	The same	2	3.0

Electron microscope studies indicate that the oxidized layer registered on certain sites of a titanium surface previously treated and exposed for 3 min in air in a muffle furnace is not more than 0.5 – 1.0 μm thick. The sample with a single enamel coat exhibits a non-uniform (on the average 1.8 μm) occasionally discontinuous oxide layer. The sample coated with two enamel layers (the adhesive and undercoat layers) displays an oxide layer 3 μm thick, which fully and uniformly covers the titanium surface (the exposure of each layer in heat treatment was 3 min).

The study of the effect of the atmosphere in the heat treatment of enamel indicates that under evacuation the thickness of the oxidized layer increases with increasing exposure duration as much as in an air atmosphere, due to the diffusion of oxygen from the proper coating. The oxides compounds making part of the undercoat layer of a glass ceramic enamel constitute the main source of oxygen forming the contact layer on the titanium surface. Their interaction with the surface in vacuum is presumably more intense. The presence of additional oxygen in heat treatment in air does not increase the thickness of the oxidized layer (Table 1).

Thus, the use of phosphoric acid as a pickling agent for the preparation of the surface of titanium and its alloys before applying a dental enamel and the introduction of an additional operation (degreasing) increase the strength of adhesion of enamel to titanium and decelerate the emergence of a layer enriched with the products of reactions (1) and (2) on the metal. The application of a dental enamel on titanium under a multiple heat treatment produces an oxide layer firmly fixed to the metal. The use of a protective atmosphere, in particular of vacuum, does not eliminate the oxidizing processes, since the enamel oxide layer in itself is sufficiently rich in oxygen that is capable of diffusing into metal.

REFERENCES

1. *Titanium structure in Orthopedic Stomatology* [in Russian], Kniga, Perm (1997).
2. S. S. Solntsev and A. T. Tumanov, *Protective Coatings of Metals in Heating* [in Russian], Mashinostroenie, Moscow (1976).
3. E. I. Litvinova, *Metal for Enameling* [in Russian], Metallurgiya, Moscow (1975).
4. A. Ya. Sitnikova and N. S. Andrushchenko, "Use of a microanalyzer for studying the reactions of titanium with coatings," in: *Protective High-Temperature Coatings, Proceed. of 5-th All-*

Union Conf. on Heat-Resistant Coatings [in Russian], Nauka, Leningrad (1972), pp. 353 – 359.
5. U. Zvicker, *Titanium and Its Alloys* [Russian translation], Metallurgiya, Moscow (1979).
6. E. E. Stashevich and I. Ya. Guzman, "Methods for determining the strength of adhesion of dental porcelain to an alloy," *Steklo Keram.*, No. 3, 30 – 31 (1984).
7. E. Voβ, "Phosphatierung — ein neues verfahren für die direktweiβemaillierung," *Mitt. Ver. Dtsch. Emailfachleute Dtsch. Email-Zentrums*, **43**(8), 101 – 106 (1995).
8. V. B. Kul'met'eva and S. E. Porozova, "Enamel coatings for protection of titanium alloy VT-6 in heating," in: *Problems of Contemporary Materials and Technology, Coll. Papers No. 5* [in Russian], Perm (2000), pp. 19 – 22.